for the a_{1g} mode, which has been observed in Raman spectra at frequencies between 328 and 335 cm^{-1}.[17,19–21] However, the spacing might also be appropriate to the $\nu_6(e_u)$ stretching frequency, which has been observed in IR spectra at 313–328 cm^{-1}.[18,19,21] A very careful study done recently by Adams and Berg[26] found ν_6 frequencies of 322 and 325 cm^{-1} for the ammonium and potassium salts, respectively, which increased to 326 and 328 cm^{-1} at 20 K. This evidence is certainly suggestive of an odd-mode structure but is far from conclusive since the corresponding data for $PtCl_4^{2-}$ in the Cs_2ZrCl_6 host lattice are not available.

We have found that the complex $[Pt(bpy)Cl_2]$ at 12 K as an undoped powder also exhibits vibronic structure in luminescence. Though the resolution is far from that achieved by Patterson on $PtCl_4^{2-}$, it appears that it is the same ν(Pt–Cl) vibration which accounts for the band structure. The observed spacing of 320 cm^{-1} can be clearly identified with the lower frequency Pt–Cl stretching mode.

In the $[Pt(bpy)Cl_2]$ complex, which has approximately C_{2v} symmetry, the Pt–Cl stretch may occur symmetrically or antisymmetrically, with $V = 0$ and 1, respectively. Both are infrared active. If the analogy with $PtCl_4^{2-}$ can be constructed, then the higher of the two frequencies represents the symmetric stretching frequency, and thus the antisymmetric forms the basis for the electronic band structure. A Raman spectrum would be expected to shed some light on this assignment, but we were unable to obtain scattering using the 514-nm line of an argon ion laser (shorter wavelengths led to sample decomposition).

A substantive question with regard to the above analysis is whether d–d emission is observed in $[Pt(bpy)Cl_2]$, as we have assumed, or π^*–d emission. The question is not simply answered, but evidence for the d–d nature comes from (1) comparison with some other dichlorodiamines,[27] which have similar emission maxima, (2) a comparison with $[Pt(bpy)_2]^{2+}$, which emits at higher energy (525 nm for the perchlorate salt[28] (even in $[Pt(bpy)_2]^{2+}$, it is not clear that the emission is π^*–d), and (3) the lifetime (18 μs at 77 K)[29] of $[Pt(bpy)Cl_2]$, which is similar to those observed for other Pt(II) complexes with d–d emission.

In conclusion, the available evidence suggests that progressions in an antisymmetric ($V = 1$) stretching mode are responsible for the electronic band structure in the luminescence spectrum of $PtCl_4^{2-}$ and $Pt(bpy)Cl_2$, as predicted by the octupole selection rule of Hollebone[15] but is not yet conclusive. The present work should be taken as a stimulus to report infrared and Raman data, under as similar conditions as possible, in future vibronic (in particular, luminescence) studies of transition-metal complexes.

Acknowledgment. We are grateful to Professor H.-H. Schmidtke and Dr. Thomas Schonherr, who obtained the far-infrared spectra. We also thank the Research Corporation for their support of this work through a Cottrell Research Grant.

Registry No. $Pt(bpy)Cl_2$, 13965-31-6; $PtCl_4^{2-}$, 13965-91-8.

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Syntheses of Iron Carbonyl Trimethylsilanes: Preparations and Interconversions of *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$, $M^+[(CO)_4FeSi(CH_3)_3]^-$, and *trans*-$[-Fe(CO)_4Si(CH_3)_3]_2$

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Reaction of petroleum ether slurries of $M_2Fe(CO)_4$ (M = Na, K) with $(CH_3)_3SiBr$ results in ca. 50% yields of *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (**1**). When $K_2Fe(CO)_4$ is reacted with $(CH_3)_3SiBr$ for 0.5 h in THF, fair yields of $K^+[(CO)_4FeSi(CH_3)_3]^-$ (**2a**) are obtained. Reaction of $(CO)_4Fe(H)Si(CH_3)_3$ with KH and NaH affords **2a** (90%) and $Na^+[(CO)_4FeSi(CH_3)_3]^-$ (**2c**; 68%), respectively. Both **2a** and **2c** are oxidized by $C_7H_7^+PF_6^-$ to the labile binuclear complex *trans*-$[-Fe(CO)_4Si(CH_3)_3]_2$ (**3**). Complex **3** can be independently generated from **1** and benzaldehyde and is reduced by Na/Hg to **2c**. Other reactions and interconversions of these silanes are described. Some earlier unsuccessful attempts to prepare **1** by related routes are discussed.

Introduction

(Trimethylsilyl)- and (trialkylsilyl)iron carbonyl complexes are finding increasing application in organic and organometallic synthesis.[1–3] Consequently, we have sought to synthesize new complexes in this series that may have useful properties. In this paper, we describe syntheses and interconversions of the iron trimethylsilanes *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (**1**), $M^+[(CO)_4FeSi(CH_3)_3]^-$ (M^+: K^+, **2a**; $[(C_6H_5)_3P]_2N^+$, **2b**; Na^+, **2c**; $[(C_2H_5)_2N]_3S^+$, **2d**), and *trans*-$[Fe(CO)_4Si(CH_3)_3]_2$ (**3**). Although **1** is a known compound, the preparation herein represents a distinct improvement of the literature procedure[4] and is of interest in view of the history of this molecule (vide infra).[5–7] A portion of this

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† Fellow of the Alfred P. Sloan Foundation (1980–1982) and Camille and Henry Dreyfus Teacher-Scholar grant recipient (1980–1985).

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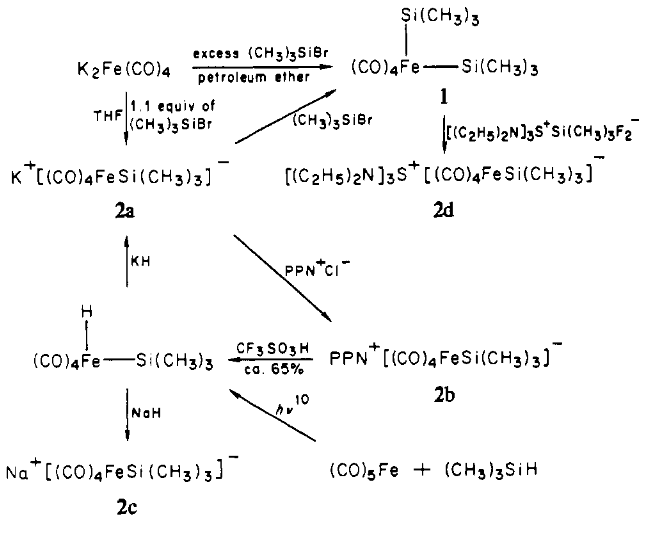

Scheme I. Syntheses and Interconversions of Mononuclear Iron Trimethylsilanes

work has been communicated.[2]

Results

Petroleum ether slurries of readily available $K_2Fe(CO)_4$[8] or $Na_2Fe(CO)_4 \cdot 1.5$diox (diox = dioxane)[9] were reacted with excess $(CH_3)_3SiBr$ for periods of 4–5 days. Sublimation of the reaction residue afforded *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ in 45–55% yields. Spectral properties (Experimental Section) were in good agreement with those previously reported by Graham.[4]

Partial silylation of $K_2Fe(CO)_4$ was effected by reaction (as a THF slurry) with 1.1 equiv of $(CH_3)_3SiBr$ for 0.5 h at 0 °C. Ether extraction of the reaction residue afforded a new iron silane (yield of crude product ca. 55%) whose spectral properties (Experimental Section) indicated it to be $K^+[(CO)_4FeSi(CH_3)_3]^-$ (**2a**). Metathesis with $[(C_6H_5)_3P]_2N^+Cl^-$ (PPN^+Cl^-) afforded white, air-stable $PPN^+[(CO)_4FeSi(CH_3)_3]^-$ (**2b**). Spectral properties of **2b** were similar to those of **2a**, and microanalysis (Experimental Section) unequivocally established its composition. For the provision of further data on the identity of these anionic trimethylsilanes, a petroleum ether slurry of **2a** was allowed to react with $(CH_3)_3SiBr$ (1.5 equiv) for 60 h. Sublimation of the reaction residue afforded *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (**1**) in 76% yield. Summaries of these and some following transformations are provided in Scheme I.

Hydride $(CO)_4Fe(H)Si(CH_3)_3$ was prepared by the photolysis of $Fe(CO)_5$ in the presence of $(CH_3)_3SiH$, as described by Wrighton.[10] Subsequent in situ reaction with KH (0.5 h, 0 °C) and workup afforded $K^+[(CO)_4FeSi(CH_3)_3]^-$ (**2a**; 90% yield from $Fe(CO)_5$) of better purity than that obtained from the partial silylation of $K_2Fe(CO)_4$. However, trace amounts of a deep red impurity (which did not interfere with subsequent alkylation reactions)[2] could not be removed. Similar treatment of $(CO)_4Fe(H)Si(CH_3)_3$ with NaH afforded, in a much slower reaction (5.5 h, 0 °C), $Na^+[(CO)_4FeSi(CH_3)_3]^-$ (**2c**) as a white powder in 68% yield.

The protonation of $PPN^+[(CO)_4FeSi(CH_3)_3]^-$ (CD_2Cl_2, −40 °C) with CF_3SO_3H (1.0 equiv) was attempted. By ^1H NMR, some $(CO)_4Fe(H)Si(CH_3)_3$ was observed to form (δ 0.54, −9.53;[10] 65% relative to internal standard). However, several byproducts were evident (e.g., δ −9.62, believed to be $(CO)_4FeH_2$[11]).

We sought to determine if $M^+[(CO)_4FeSi(CH_3)_3]^-$ species could be prepared from *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (**1**). Reaction of **1** with PPN^+Cl^- did not lead to **2b**. However, reaction of **1** with $[(C_2H_5)_2N]_3S^+\,Si(CH_3)_3F_2^-$[12] yielded $[(C_2H_5)_2N]_3S^+[(CO)_4FeSi(CH_3)_3]^-$ (**2d**) as a brown oily solid. Previously, $[(C_2H_5)_2N]_3S^+\,Si(CH_3)_3F_2^-$ has been shown to be an excellent anhydrous F^- source that rapidly cleaves silicon–oxygen bonds.[12]

The synthesis of the binuclear trimethylsilane $[-Fe(CO)_4Si(CH_3)_3]_2$ (**3**) was attempted next. Methylene chloride slurries of $Na^+[(CO)_4FeSi(CH_3)_3]^-$ or $K^+[(CO)_4FeSi(CH_3)_3]^-$ were reacted with tropylium hexafluorophosphate ($C_7H_7^+PF_6^-$). Careful fractional sublimation of the reaction residue afforded a material (ca. 40% yield) whose spectral properties (Experimental Section; two principal $\nu_{C\equiv O}$ resonances and one ^{13}C NMR carbonyl resonance to −40 °C)[13,14] were consistent with its formulation as *trans*-$[-Fe(CO)_4Si(CH_3)_3]_2$ (**3**). This compound proved to be exceedingly labile (sensitive to O_2, H_2O, and ethereal solvent vapors; gradual decomposition at 25 °C), but its identity was supported by additional observations. First, **3** underwent reductive cleavage to **2c** in 65% isolated yield when treated with Na/Hg in petroleum ether. Second, **3** was independently generated (in situ) by homolysis of the organometallic adduct $[(CH_3)_3Si](CO)_4Fe-CH(C_6H_5)OSi(CH_3)_3$ (**4**, Scheme II).[1a] Previously, we demonstrated the similar homolysis of $(CO)_5Mn-CH(C_6H_5)OSi(CH_3)_3$ to symmetrical dimers $[(CO)_5Mn]_2$ and $[-CH(C_6H_5)OSi(CH_3)_3]_2$.[1] Finally, ruthenium and osmium homologues of **3** have been prepared by Stone and Knox,[13] and iron–tin compounds of the formula $[Fe(CO)_4SnR_3]_2$ (R = CH_3, C_6H_5) have been synthesized.[14] In every case, spectroscopic data have indicated trans stereochemistry for these binuclear complexes.

Discussion

An interesting history surrounds the synthesis of *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (**1**). The reaction of $Na_2Fe(CO)_4$ with $(CH_3)_3SiI$ in THF was initially reported by MacDiarmid and co-workers to yield a compound of empirical formula $(CO)_4Fe[Si(CH_3)_3]_2$ in 27% yield.[5,6] Molecular weight measurements and spectral data prompted formulation of the product as the tetrahedral species **5** (Scheme III). It was also claimed that **5** (but not **1**) formed when a hexane slurry of THF-free $Na_2Fe(CO)_4$ reacted with $(CH_3)_3SiI$. Subsequently, Graham reinvestigated this reaction utilizing $(CH_3)_3SiBr$ and demonstrated MacDiarmid's product to have the structure **6** (Scheme III), which is devoid of metal–silicon bonds.[7] In a later paper, Graham reported the synthesis of authentic **1** in 36% yield via the photochemical reaction of $Fe(CO)_5$ and $Hg[Si(CH_3)_3]_2$.[4]

In light of the above background, our synthesis of **1** from $K_2Fe(CO)_4$ (Scheme I) and $Na_2Fe(CO)_4$ has both mechanistic and preparative significance. Although the Graham–MacDiarmid product **6** lacks iron–silicon bonds, our data demonstrate that it is possible to trimethylsilylate $(CO)_4Fe^{2-}$ at iron. Interestingly, we also find that **1** is formed (up to 30%) when a petroleum ether slurry of $Na_2Fe(CO)_4$ is reacted with $(CH_3)_3SiI$; we suggest that **1** was accidentally volatilized under the MacDiarmid workup conditions.[6] Since we prepare **2a** in THF (and can observe the formation of some **2c** when $Na_2Fe(CO)_4 \cdot 1.5$diox is treated with $(CH_3)_3SiBr$ in THF),

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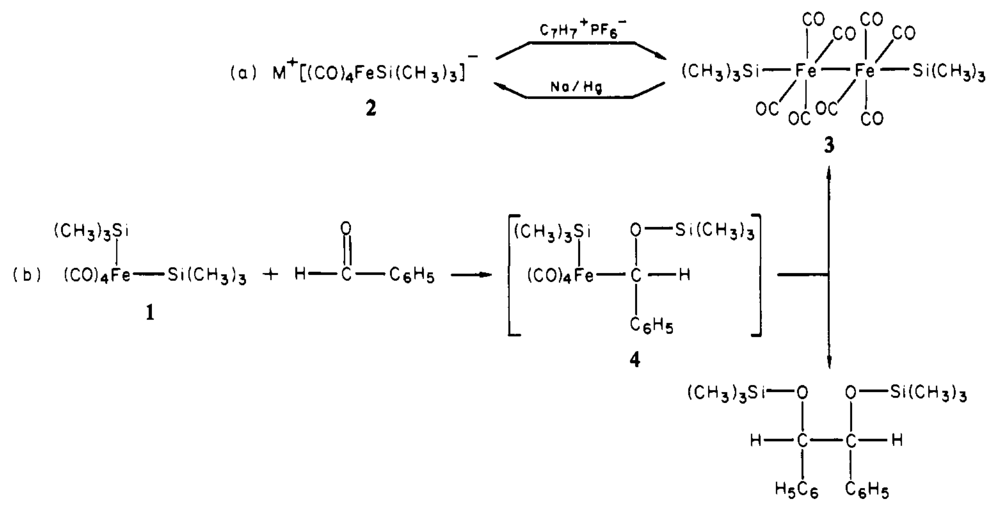
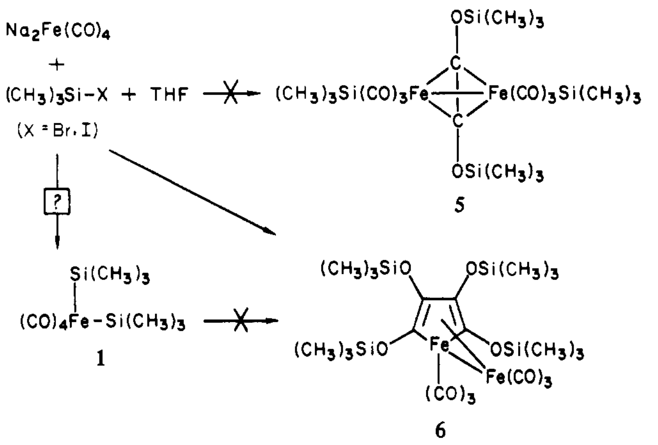
Scheme II. Syntheses of the Binuclear Iron Trimethylsilane 3



Scheme III



some iron silylation is almost certainly occurring under the Graham–MacDiarmid conditions. However, **1** (which is reactive toward ethers in general)[3] decomposes in THF immediately[4] and would not be expected to survive the reaction. Similarly, **2a** is THF sensitive (decomposition over 24 h at 25 °C), and any $[(CO)_4FeSi(CH_3)_3]^-$ remaining upon solvent removal from the Graham–MacDiarmid reactions would not be subsequently isolated via the sublimation procedures employed. Since Graham has previously noted that **1** does not decompose to **6** in THF (and identical results have been obtained in our laboratory from similar experiments conducted in the presence of NaBr), it seems likely that two distinct initial modes of $(CO)_4Fe^{2-}$ attack upon $(CH_3)_3Si$–X occur in THF. Significant quantities of **6** are not formed from $(CO)_4Fe^{2-}$ and $(CH_3)_3Si$–X in hydrocarbon solvents, as judged from IR spectra of residues remaining after the sublimation of **1**.

Since the use of sensitive and difficulty prepared $Hg[Si(CH_3)_3]_2$ is avoided and byproducts are easily separated, we believe our synthesis of **1** to be the method of choice. This route is modeled after earlier metal silane syntheses of Malisch.[15] He found that hydrocarbon slurries of transition-metal anions reacted with numerous R_3Si–X species to give L_nM–SiR_3 complexes.[15] The driving force for these reactions, which are probably not very exothermic, is thought to be the precipitation of a salt with a good lattice energy such as KBr.

The $M^+[(CO)_4FeSi(CH_3)_3]^-$ systems prepared are closely related to $[(CO)_4FeSiX_3]^-$ ($X = Cl$, C_6H_5) species previously described by Kruck[16] and Graham.[17] The primary impetus for the synthesis of **2a**–**d** derives from the fact that M–$Si(CH_3)_3$ complexes show considerably more reactivity than other M–SiR_3 or M–SiX_3 complexes toward oxygen-containing organic compounds.[1,3,15,18] These anions can be used to prepare iron alkyls of the formula *cis*-$(CO)_4Fe(R)Si(CH_3)_3$,[2] and other facets of their chemistry are under intensive study. Counterions can play an important role in metal anion reactivity;[9a] for most synthetic purposes, **2a** and **2c** give the best results. However, whereas **2a** and **2c** decompose in minutes in air, PPN^+ salt **2b** is stable for days. Compound **2d** shows only moderate decomposition after several hours in air.

Knox and Stone have previously attempted the protonation of $[(CO)_4MSi(CH_3)_3]^-$ (M = Ru, Os) anions.[13] For M = Ru, formation of a ruthenium hydride was *not* observed; with M = Os, $(CO)_4Os(H)Si(CH_3)_3$ was isolated in only 25% yield. Thus it is not surprising that **2b** is not cleanly protonated to $(CO)_4Fe(H)Si(CH_3)_3$ (Scheme I).

Carbonyls $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ undergo reaction with $(CH_3)_3SiH$ at 80–140 °C to form (among other products) *trans*-$[-Ru(CO)_4Si(CH_3)_3]_2$ and *trans*-$[-Os(CO)_4Si(CH_3)_3]_2$, respectively.[13] It is not practical to similarly prepare iron silane **3**, however, since it is by no means robust enough to survive such conditions. There exist many examples of second- and third-row transition-metal complexes that show greater thermal stability than their first-row homologues.

When **3** is synthesized by route a in Scheme II, the byproduct bitropyl is sufficiently volatile to be sublimed from the product. However, the silylated pinacol ether formed in route b (Scheme II) is not easily separated from **3**. By use of a higher molecular weight aldehyde than benzylaldehyde in route b, this difficulty might be overcome.

The reaction of **1** and benzaldehyde to yield **4** in the initial step of route b constitutes a novel metal–carbon bond-forming reaction. We have recently detailed the mechanism and scope of the analogous reaction of $(CO)_5Mn$–$Si(CH_3)_3$ with aldehydes.[1b] However, since iron α-silyloxyalkyls such as **4** undergo rapid metal–carbon bond homolysis at room temperature, this reaction is of limited use for the synthesis of iron alkyls.

In summary, we have described procedures by which several iron carbonyl trimethylsilanes can be systematically and rationally prepared. Their utility in organic and organometallic synthesis is under active investigation.

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Experimental Section

General Comments. All reactions and distillations were conducted with the rigorous exclusion of air and water. Petroleum ether (bp 20–40 °C) and CH_2Cl_2 were distilled from $LiAlH_4$ and P_2O_5, respectively. Acetone was distilled from K_2CO_3 and $KMnO_4$ or treated with freshly activated 4-Å molecular sieves. The above solvents were also freeze–pump–thaw degassed before use. THF and $(C_2H_5)_2O$ were distilled from Na/benzophenone under N_2.

$(CH_3)_3SiH$ and $(CH_3)_3SiBr$ were obtained from Petrarch. $(CH_3)_3SiH$ was used without purification; $(CH_3)_3SiBr$ was refluxed overnight over CaH_2, distilled, and freeze–pump–thaw degassed before use. Tropylium hexafluorophosphate and $Fe(CO)_5$ were obtained from Aldrich and used without purification. $K_2Fe(CO)_4$ and $Na_2Fe(CO)_4{\cdot}1.5$diox were prepared by published procedures.[8,9b] PPN^+Cl^- was synthesized by the method of Ruff.[19] $[(C_2H_5)_2N]_3S^+Si(CH_3)_3F_2^-$ was prepared as described by Middleton.[12b]

^1H NMR spectra were obtained on a Varian T-60 spectrometer unless noted. ^{13}C NMR spectra were recorded on Bruker WP-200 and Varian CFT-20 spectrometers. IR spectra were obtained on a Perkin-Elmer 521 spectrometer. Microanalyses were conducted by Schwartzkopf.

Preparations of *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (1). A. A slurry of $K_2Fe(CO)_4$ (1.8 g, 7.3 mmol) and $(CH_3)_3SiBr$ (6 mL, 45.8 mmol in 50 mL of petroleum ether (bp 20–40 °C) was stirred for 4 days. The reaction mixture was filtered, and the solvent was removed from the filtrate under reduced pressure. A colorless solid, contaminated with a red-brown oil, was obtained. Sublimation (25 °C, 0.1 mm, dry ice cooled probe) yielded 1.15 g (50% based upon $K_2Fe(CO)_4$) of colorless **1**, spectroscopically similar (IR (cm^{-1}, hexane) 2068 m, 1999 s, 1978 vs, 1963 s, sh; ^1H NMR (δ, C_6D_6) 0.49) to **1** previously reported by Graham.[7]

B. A slurry of $Na_2Fe(CO)_4{\cdot}1.5$diox (3.4 g, 10 mmol) and $(CH_3)_3SiBr$ (4 mL, 4.7 g, 30 mmol) in 10 mL of petroleum ether (bp 20–40 °C) was stirred for 5 days. The reaction mixture was then diluted with 25 mL of petroleum ether and filtered. The solvent was removed from the filtrate under reduced pressure. The red solid residue was sublimed as above to give colorless needles of **1** (1.67 g, 5.3 mmol, 53%).

Preparations of $K^+[(CO)_4FeSi(CH_3)_3]^-$ (2a). A. To a stirred slurry of $K_2Fe(CO)_4$ (3.0 g, 12.2 mmol) in 40 mL of THF at 0 °C was added (dropwise) 2.05 g (13.4 mmol) of $(CH_3)_3SiBr$ in 5 mL of THF. After being stirred for 0.5 h, the slurry was filtered and the THF removed under reduced pressure. The residue was washed 3 times with petroleum ether and then extracted with $(C_2H_5)_2O$. After filtration, $(C_2H_5)_2O$ was removed under vacuum to yield 1.9 g of **2a** as a deep red solid (56% crude yield): IR (cm^{-1}, THF) 1980 m, 1887 s, 1872 s, 1832 m; ^1H NMR (δ, acetone-d_6) 0.34; ^{13}C NMR (ppm, acetone-d_6) 221.3, 8.0. When an internal standard was added in the ^1H NMR spectrum, integration indicated a purity of 75%.

B. A 50-mL glass tube was charged with a solution of 1.14 g (5.8 mmol) of $Fe(CO)_5$ in 15 mL of petroleum ether, capped with a septum, and cooled to 0 °C. $(CH_3)_3SiH$ (3.0 g, 40.4 mmol) was added to the solution via an inlet needle inserted through the septum. This needle was removed and replaced with one attached via an adapter to a balloon. The tube was immersed in an ice bath in a pyrex Dewar flask and irradiated through the Dewar flask for 8 h in a 350-nm Rayonet reactor. CO pressure was relieved via the balloon. After irradiation was completed, the solution was transferred via a double-ended needle into a 250-mL round-bottomed flask containing $(C_2H_5)_2O$ (60 mL) and KH (349 mg, 8.7 mmol) at 0 °C. The tube was washed with 10 mL of $(C_2H_5)_2O$, which was also transferred to the flask. The reaction slurry was stirred for 0.5 h and then vacuum-filtered. Removal of solvent under reduced pressure gave 1.47 g (90%) of white **2a** containing trace amounts of a deep red impurity. Efforts to remove this impurity (petroleum ether insoluble) were not successful, but it did not adversely affect subsequent alkylation reactions[2] of **2a**.

Preparation of $PPN^+[(CO)_4FeSi(CH_3)_3]^-$ (2b). PPN^+Cl^- (974 mg, 1.70 mmol) in 20 mL of acetone was added to a solution of **2a** (500 mg, 1.78 mmol) in 15 mL of acetone. After being stirred for 0.5 h, the slurry was filtered and the solvent removed under reduced pressure. The residue was washed twice with $(C_2H_5)_2O$ and then dissolved in a minimal amount of THF. $(C_2H_5)_2O$ was then added slowly until some precipitation occurred. The solution was filtered and the filtrate cooled by evaporation of some $(C_2H_5)_2O$; the volume was maintained by the occasional addition of $(C_2H_5)_2O$ (this process is carried out in a glove box, where cold baths cannot be used). The precipitate was collected by filtration. Most of the solvent was removed from the filtrate and the above THF/$(C_2H_5)_2O$ precipitation process repeated to give a total of 920 mg of pink-brown solid. This process was repeated 5–7 times using THF/$(C_2H_5)_2O$ or CH_2Cl_2/$(C_2H_5)_2O$; the final filtrate was discarded in each cycle. Thus obtained was 700 mg (71%) of white, air-stable **2b**: mp 185–187 °C (some decomposition); IR (cm^{-1}, THF) 1984 m, 1888 s, 1863 vs; ^1H NMR (δ, acetone-d_6) 0.37. Anal. Calcd for $C_{43}H_{39}FeNO_4P_2Si$: C, 66.24; H, 5.04; Fe, 7.16; N, 1.80; P, 7.45; Si, 3.60. Found: C, 65.95; H, 5.21; Fe, 6.86; N, 2.02; P, 7.73; Si, 3.24.

Preparation of $Na^+[(CO)_4FeSi(CH_3)_3]^-$ (2c). A solution of $Fe(CO)_5$ (1.15 g, 5.87 mmol) and $(CH_3)_3SiH$ (3.33 g, 44.88 mmol) in 15 mL of petroleum ether was photolyzed and transferred as described in procedure B for **2a**. NaH (0.211 g, 8.80 mmol) was used in place of KH. The slurry was stirred to 0 °C for 5.5 h and the purple solution filtered. The flask was rinsed with $(C_2H_5)_2O$ to dissolve some white crystalline material that precipitated. These washings were filtered and combined with the above filtrate, which was then cooled by evaporation of $(C_2H_5)_2O$ under reduced pressure. White crystals precipitated, which were collected by suction filtration and washed with small amounts of cold $(C_2H_5)_2O$; the washings were returned to the mother liquor. After several additional crops, the product was dried under vacuum (transforming from crystals to a powder) to give white **2c** (1.06 g) in 68% yield: IR (cm^{-1}, THF) 1991 m, 1896 s, sh, 1865 s, 1837 m; ^1H NMR (δ, acetone-d_6) 0.36; ^{13}C NMR (ppm, acetone-d_6) 221.3, 8.1.

Preparation of $[(C_2H_5)_2N]_3S^+[(CO)_4FeSi(CH_3)_3]^-$ (2d). To 250 mg (0.69 mmol) of $[(C_2H_5)_2N]_3S^+Si(CH_3)_2F_2^-$ was added 245 mg (0.77 mmol) of **1** in 10 mL of benzene. After 5 min of stirring, most of the benzene was pipetted away from a dark brown insoluble oil. The remaining benzene was removed under reduced pressure, and the oil was washed with petroleum ether, dissolved in CH_2Cl_2, and filtered. Removal of the CH_2Cl_2 under reduced pressure afforded 340 mg (100% crude yield) of **2d** as an oily brown solid: IR (cm^{-1}, THF) 1983 m, 1887 s, sh, 1859 s; ^1H NMR (δ, acetone-d_6) 3.37 (q, J = 7 Hz, 12 H), 1.28 (t, J = 7 Hz, 18 H), 0.36 (s, 9 H).

Reaction 2a with $(CH_3)_3SiBr$. A slurry of **2a** (250 mg, 0.89 mmol) and $(CH_3)_3SiBr$ (205 mg, 1.34 mmol) in petroleum ether (20 mL) was vigorously stirred for 60 h. The reaction was filtered and the solvent removed under reduced pressure. Sublimation as described above afforded 212 mg (76%) of **1**.

Reaction of 2b with CF_3SO_3H. A 5-mm NMR tube was charged with **2b** (71 mg, 0.091 mmol), hexamethylbenzene standard (3.7 mg, 0.023 mmol), and CD_2Cl_2 (0.5 mL) and was fitted with a septum. After the tube was cooled to −40 °C and a ^1H NMR spectrum (200 MHz) was recorded, CF_3SO_3H (8 μL, 0.091 mmol) was added. Resonances, which were assigned to $(CO)_4FeHSi(CH_3)_3$ (65% vs. hexamethylbenzene), appeared at δ 0.54 and −9.53 (ca. 9:1);[10] other resonances appeared at δ −9.62 (believed to be $(CO)_4FeH_2$)[11] and 0.11. After 0.33 h, the sample was warmed to −10 °C; after an additional 1.25 h, the sample was warmed to 10 °C. At this temperature, $(CO)_4FeHSi(CH_3)_3$ slowly decomposed and the δ 0.11 resonance increased. No $(CH_3)_3SiH$ appeared.

Syntheses of *trans*-$[-Fe(CO)_4Si(CH_3)_3]_2$ (3). A. A flask was charged with CH_2Cl_2 (25 mL), **2c** (250 mg, 0.95 mmol), and $C_7H_7^+PF_6^-$ (246 mg, 1.04 mmol). After 35 min of stirring, CH_2Cl_2 was removed under reduced pressure. The residue was extracted with petroleum ether, and the extracts were filtered. The petroleum ether was evaporated under reduced pressure and the residue fractionally sublimed at 25 °C and 4×10^{-4} mm. The first two fractions contained mainly $C_{14}H_{14}$. The third fraction consisted of pure bright yellow **3** (93 mg, 41%): IR (cm^{-1}, petroleum ether) 2035 m, 2019 s; ^1H NMR (δ, C_6D_6) 0.46; ^{13}C NMR (ppm, C_6D_6, 7 °C) 212.5, 7.3; ($C_6D_5CD_3$, −40 °C) 212.9 (slightly broadened), 7.2.

Both **2a** and **2b** could also be used to prepare **3** in comparable yields, but IR spectra of sublimed product indicated minor amounts of impurities to be present.

B. A 5-mm NMR tube was charged with 165 mg (0.53 mmol) of **1** and sealed with a latex septum. C_6D_6 (0.5 mL) was injected, and the tube was cooled to 5 °C in the probe of an A-60 ^1H NMR spectrometer. Benzaldehyde (50 μL, 53 mg, 0.50 mmol) was added by syringe and the formation of **4** (Scheme II) monitored. After 1

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h, resonances attributable to 4^{1a} were at a maximum. The sample was then warmed to room temperature; after 1 h, **3** (δ 0.60, s, 18 H) was present in 85% yield (relative to total phenyl protons). An aliquot was diluted with heptane for an IR spectrum: 2027 m, 2013 s cm^{-1}. A similar experiment was conducted to obtain a ^{13}C NMR spectrum (ppm, C_6D_6): 212.4, 7.2.

Reaction of 3 with Na/Hg. Petroleum ether (30 mL) containing **3** (68 mg, 0.14 mmol) was stirring for 0.5 h over an amalgam of Na (61 mg, 2.6 mmol) and Hg (3 mL). $(C_2H_5)_2O$ (20 mL) was added and the solution decanted and filtered. The amalgam residue was washed with additional $(C_2H_5)_2O$ and filtered. Solvent was removed from the combined filtrates to yield **2c** (48 mg, 64%) as a light pink powder.

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Registry No. 1, 53248-31-0; **2a**, 78240-74-1; **2b**, 78465-74-4; **2c**, 79483-28-6; **2d**, 79483-29-7; **3**, 79483-30-0; $K_2Fe(CO)_4$, 16182-63-1; $Na_2Fe(CO)_4$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; $(CH_3)_3SiBr$, 2857-97-8; $(CH_3)_3SiH$, 993-07-7; CF_3SO_3H, 1493-13-6; $(CO)_4FeH$-$Si(CH_3)_3$, 63022-27-5.

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Electronic Structure of Metal Clusters. 1. Photoelectron Spectra and Molecular Orbital Calculations on (Alkylidyne)tricobalt Nonacarbonyl Clusters

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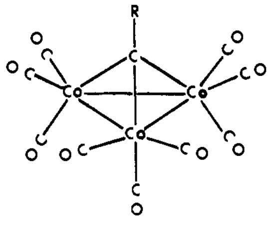
Ultraviolet photoelectron (PE) spectra and molecular orbital (MO) calculations are reported for several (alkylidyne)tricobalt nonacarbonyl compounds, $RCCo_3(CO)_9$, where R = H, CH_3, OCH_3, Cl, Br, and I. The molecular ionization energies from the PE spectra are closely related to the valence-orbital electronic structure. The MO calculations are helpful in assigning the spectra, in confirming the interpretation of trends, and in providing a consistent description of the electronic structure. The lowest energy ionization corresponds to a delocalized orbital which is both Co–C and Co–Co bonding. This ionization is followed closely by bands due to the Co–Co bonds and Co–CO π bonds. Well separated from these ionizations are those which correspond to Co–C bonding orbitals. The origin of this molecular orbital pattern is described both as the joining of three $Co(CO)_3$ fragments with a RC fragment and as the perturbation of a CCo_3 cluster by nine CO ligands and one R ligand. Although both descriptions are equally valid, the former provides a simpler interpretation of the MO results and PE spectra. Comparison of the PE spectra of H_3CX, $HC{\equiv}CX$, C_6H_5X, and $(CO)_9Co_3CX$ for the halogens suggests that the π bonding of the cobalt cluster to the apical C is much closer to $HC{\equiv}CX$ or C_6H_5X than it is to H_3CX. Both the PE spectra and MO calculations suggest that the apical carbon is electron rich but that the π system is sufficiently flexible to act as either a donor or acceptor. A localized MO description with an sp-hybridized C, in which a lone pair forms a dative bond to the metal triangle and the remaining p orbitals form multicentered π bonds to the Co_3 system, is consistent with all experimental evidence. If these ideas are extended to other systems, the hybridization at any carbon atom is determined primarily by the geometry of its non-transition-metal substituents. Thus, the CR group is best described as sp hybridized regardless of whether it is bound to a single metal or bridging three metals.

Introduction

The (alkylidyne)tricobalt nonacarbonyls are the oldest examples of heteronuclear cobalt carbonyl clusters.[1] Of all organometallic clusters, these have the most thoroughly explored organic chemistry.[2] Several review articles[2a,3] which cover both chemical and structural properties have appeared. Apart from the interest in their organic chemistry, suggestions have been made that discrete metal clusters may serve as models for miniature metal surfaces or highly dispersed, supported catalysts.[4]

The first crystal structure,[5] which was of $CH_3CCo_3(CO)_9$, confirmed a geometry consisting of a triangle of cobalts each with three carbonyls, capped by the CH_3C group, **1**. Simple



1

electron counting shows that the cluster is electron precise and the bonding can be described as 2-center, 2-electron bonds between atoms in the Co_3C core. Such a bonding picture is shown in **2**, where each line represents a 2-electron bond, and suggests an apical carbon with sp^3 hybridization.

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